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(54) 【発明の名称】 リチウム二次電池

(57) 【要約】

【課題】 従来のリチウムイオン二次電池においては薄型化に一定の限界があった。

【解決手段】 負極体の体積膨張率 (リチウムイオン吸蔵時とリチウムイオン放出時との体積比) が正極体よりも大きく、かつ該負極体の厚みを、放電時を基準として該正極体の厚みの半分以下とすることにより、さらに薄型リチウム二次電池を提供可能である。

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# PATENT ABSTRACTS OF JAPAN

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## (54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To make a battery thin by setting a coefficient of cubic expansion (the volume ratio of lithium ion storing time to lithium ion release time) of a negative electrode body larger than a positive electrode body, and setting a thickness of the negative electrode body not more than half the thickness of the positive electrode body with discharge time as a reference.

SOLUTION: In a lithium secondary battery, while a positive electrode body desirably includes lithium containing oxide of one metal selected from a group composed of cobalt, manganese and nickel, a negative electrode body includes one selected from among a group composed of tin oxide, silicon oxide, lithium transition metal composite nitride and a silicon/carbon complex, and includes a silicon/carbon composite baking body obtained by heat-treating silicon or the compound in the presence of an organic material or a carbon material, and the negative electrode body is a sintered body having a thickness of 20 to 500  $\mu\text{m}$  or a paint film body which has a thickness of 20 to 150  $\mu\text{m}$ . Thus, storing/releasing quantity of a lithium ion and a superior cycle characteristic in the same as the conventional cases can be obtained, while thinning the battery.

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## CLAIMS

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[Claim(s)]

[Claim 1] The lithium secondary battery characterized by for the coefficient of cubical expansion (volume ratio with the time of lithium ion occlusion and lithium ion emission) of said negative-electrode object to have been larger than said positive-electrode object, and to make thickness of this negative-electrode object below one half of the thickness of this positive-electrode object on the basis of the time of discharge in the lithium secondary battery which arranges a negative-electrode object and a positive-electrode object through an ionic conduction layer, carries out the laminating of this, or winds it, and it comes to seal in a container.

[Claim 2] The lithium secondary battery according to claim 1 with which said negative-electrode object contains one chosen from the group which consists of ZUZU oxide, silicon oxide, a lithium transition-metals compound nitride, and silicon / carbon composite while said positive-electrode object contains the lithium content oxide of one metal chosen from the group which consists of cobalt, manganese, and nickel.

[Claim 3] The lithium secondary battery according to claim 2 with which said negative-electrode object contains the silicon / carbon compound baking object which heat-treats silicon or its compound under existence of an organic material or a carbon material, and is obtained.

[Claim 4] The lithium secondary battery according to claim 1 said whose negative-electrode object is a sintering object with a thickness of 20-500 micrometers or a paint film object with a thickness of 20-150 micrometers.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to amelioration of a thin lithium secondary battery.

[0002]

[Description of the Prior Art] Since a lithium secondary battery can attain the highest energy density in an existing rechargeable battery, it is most expected as what fills the request of the formation of a rechargeable battery high energy consistency accompanying the formation of small lightweight of a portable electronic device, and thin shape-ization is advanced.

[0003] As a negative-electrode object ingredient of a lithium secondary battery, carbon materials, such as a graphite in which current, and the occlusion and emission of a lithium ion are possible, are used most widely. the electromotive force at the time of the lithium content transition-metals oxide which can emit [ occlusion and ] a lithium ion being used generally as a positive-electrode ingredient on the other hand, and considering as a cell especially -- large -- high energy -- a consistency -- the cobalt acid lithium [ -izing / the lithium ] is used most widely. To per unit volume, since occlusion and the

amount of lithium ions to emit were almost equivalent, in the conventional lithium secondary battery, the thickness of a negative-electrode object and a positive-electrode object of the carbon material which is a negative-electrode object, and the lithium content transition-metals oxide which is a positive-electrode object was almost equivalent.

[0004]

[Problem(s) to be Solved by the Invention] The great portion of thickness of a lithium secondary battery is occupied with the positive-electrode object and the negative-electrode object. Therefore, although it is most effective for the formation of a lithium secondary battery thin shape to decrease the thickness of an electrode object, it is necessary to increase the lithium ion occlusion and the burst size per electrode object unit volume for that purpose. However, since the lithium content transition-metals oxide conventionally used for a positive-electrode object had the theoretically fixed amount of the lithium ion which can carry out occlusion during a crystal, the steep increment in the amount of lithium ion occlusion was difficult. Moreover, in the crystalline graphite system carbon material, the carbon material used as a negative-electrode object also had a limitation, and the increment in the amount of lithium ion occlusion was theoretically difficult for it in the field where current density is high in the amount of lithium ion occlusion also in the pitch system carbon material made amorphous. That is, in the above-mentioned conventional rechargeable lithium-ion battery, the fixed limitation was in thin shape-ization.

[0005] However, as a result of examination, by replacing with a carbon material about a negative-electrode object, and changing into an ingredient with a bigger coefficient of cubical expansion than a positive-electrode object, the steep increment of lithium ion occlusion and the burst size was carried out, and many things were understood that thickness reduction of an electrode object is possible. For example, the stannic-acid ghost (JP,07-263028,A), the silicon oxide (JP,06-325765,A), the lithium transition-metals compound nitride (JP,09-102311,A), the silicon / carbon composite (WO 98/No. 24135), etc. are reported as such an ingredient, and the lithium ion occlusion and emission of the more than twice of a positive electrode are possible for each of these.

[0006]

[Means for Solving the Problem] In this invention, in the lithium secondary battery, the coefficient of cubical expansion (volume ratio with the time of lithium ion occlusion and lithium ion emission) of a negative-electrode object was larger than the positive-electrode object, and it found out that thin-shape-izing of a lithium secondary battery was possible by making thickness of a negative-electrode object below into one half of the thickness of a positive-electrode object on the basis of the time of discharge.

[0007]

[Embodiment of the Invention] This invention uses an ingredient with a big coefficient of cubical expansion as a negative-electrode object as compared with a positive-electrode object ingredient, and makes it the thickness below one half of a positive-electrode object on the basis of the time of discharge. This negative-electrode object and a positive-electrode object are arranged through an ionic conduction layer, the laminating of this is carried out, or it is wound, it seals in a container, and a thin lithium secondary battery is offered.

[0008] Common lithium ion occlusion and emission ingredient can be used for the positive-electrode object ingredient of this invention, for example, the lithium content

oxide of transition metals and the metal acid lithium which makes cobalt, nickel, or manganese a metallic element preferably can be used for it.

[0009] On the other hand, as compared with a positive-electrode object, an ingredient with a high coefficient of cubical expansion can be used for a negative-electrode object ingredient, for example, a stannic-acid ghost, silicon oxide, a lithium transition-metals compound nitride, silicon / carbon composite, etc. can be used for it. A coefficient of cubical expansion is a volume ratio with the time of lithium ion charge and discharge. These negative-electrode object ingredients show a bigger coefficient of cubical expansion than a positive-electrode object. For example, a stannic-acid ghost, silicon oxide, a lithium transition-metals compound nitride, silicon / carbon composite, etc. show about 140 - 200% of coefficient of cubical expansion to the coefficient of cubical expansion of the cobalt acid lithium which is the most common positive-electrode object being about 103%.

[0010] By using an ingredient with the big coefficient of cubical expansion accompanying lithium ion charge and discharge, it becomes possible to increase the lithium ion occlusion and the burst size per unit volume of a negative-electrode object, and to perform thin shape-ization of a negative electrode. Compared with a positive-electrode object ingredient, occlusion and emission of a twice [ per unit volume / more than ] as many lithium ion as this are all possible for the above-mentioned negative-electrode object ingredient.

[0011] Therefore, the lithium secondary battery of this invention can maintain a capacity equivalent to the conventional cell, i.e., the occlusion and the burst size of a conventionally equivalent lithium ion, thin-shape-izing a cell by carrying out to below one half of the thick bean paste of the negative-electrode object which was conventionally equivalent to the positive-electrode object.

[0012] In addition, making thickness of a negative-electrode object below into one half of a positive-electrode object has important semantics in the formation of a cell thin shape, and coincidence also in the viewpoint which acquires a good cycle property. Although it originates in the cubical expansion and contraction of the positive-electrode object at the time of lithium ion occlusion and emission, and a negative-electrode object and the thickness of the whole cell changes, change of the whole cell thickness can cause cycle property degradation. For example, although a lithium secondary battery consists of the layered product of the separator which generally contains a positive-electrode charge collector, a positive-electrode object, and nonaqueous electrolyte or a polyelectrolyte, a negative-electrode object, and a negative-electrode charge collector, and two or more sheets of this layered product pile it up, or it is wound about and it is sealed in containers, such as a sheathing can, the electric contact between this layered product each class is maintained with the pressure from a sheathing can in many cases. Therefore, when the thickness of a cell increases by expansion of an electrode object, the big pressure from a sheathing can is applied to the above-mentioned layered product, and there is a possibility of causing the short circuit between positive-electrode object-negative-electrode objects. On the other hand, since the pressure concerning the above-mentioned layered product decreases and it becomes inadequate electric contacting between layered product each class when the thickness of a cell decreases by contraction of an electrode object, there is a possibility of causing degradation of the cycle property by the increment in cell internal resistance. Therefore, thickness change of the whole cell increases, so that a ratio [ as

opposed to the positive-electrode object thickness of the thickness of a negative-electrode object in the coefficient of cubical expansion of a negative-electrode object ] is high, when big compared with a positive-electrode object, and a cycle property deteriorates. That is, in this invention, making thickness of a negative-electrode object below into one half of a positive-electrode object has the effectiveness which controls degradation of a cell cycle property at the same time it thin-shape-izes a cell.

[0013] Moreover, although a negative-electrode object needs to have a coefficient of cubical expansion higher than a positive-electrode object in order to thin-shape-ize a cell, maintaining cell capacity, on the other hand from a viewpoint of a cycle property, it is desirable [ an object ] to have the lowest possible coefficient of cubical expansion. Among an above-mentioned negative-electrode object ingredient, though occlusion and emission of a lithium ion equivalent to other ingredients are possible, since the coefficient of cubical expansion is low, silicon / carbon composite, especially the silicon / carbon compound baking object that carried out elevated-temperature baking of this are the most desirable ingredients. The coefficient of cubical expansion of silicon / carbon compound baking object is only about 140% to each of stannic-acid ghosts, silicon oxide, and lithium transition-metals compound nitrides showing about 200% of coefficient of cubical expansion.

[0014] Moreover, silicon / carbon compound baking object shows one about 1.5 times the first time charge-and-discharge effectiveness of this as compared with a stannic-acid ghost and a silicon oxide, and handling [ in / as compared with air and water, and the lithium transition-metals compound nitride that reacts easily / a cell production process ] is easy for it. That is, silicon / carbon compound baking object is dealt with at the time of charge-and-discharge effectiveness and cell manufacture, and it can be said also from an easy viewpoint that it is a desirable negative-electrode object ingredient.

[0015] Silicon / carbon compound baking object is obtained by heat-treating a silicon ingredient in a non-oxidizing atmosphere under coexistence of an organic material or a carbon material. Although use of a silicon simple substance is desirable, the silicon compound which may change with baking to silicon may be used for a silicon ingredient, for example, ingredients, such as inorganic silicon compounds, such as silicon oxide, and silicone resin, an organic silicon compound, can be used for it. That an organic material should just be an ingredient carbonized by heat treatment, although not limited especially, urethane resin, phenol resin, polyvinylidene fluoride, etc. are mentioned, for example. To a carbon material, all of nongraphitizing carbon, such as graphitizing carbon, such as a graphite and a pitch, and glassy carbon, are usable. As for silicon / carbon compound baking object, it is desirable for carbonization to fully advance and to include neither a silicon dioxide nor silicon carbide substantially, and, for that purpose, it is desirable to heat-treat at 400-1500 degrees C under non-oxidizing atmospheres, such as nitrogen-gas-atmosphere mind. The processing of less than 400 degrees C of carbonization is inadequate, and it is because silicon carbide generates in heat treatment exceeding 1500 degrees C.

[0016] By the way, since each of above-mentioned negative-electrode objects and positive-electrode object ingredients is fine particles, they really needs to fabricate these and needs to form an electrode object. The electrode object forming method is roughly classified into a paint film method and the sintering method. A paint film method is the approach of adjusting the slurry which carried out solvent distribution of the mixture,

such as an electrode object ingredient, a binder, and electric conduction material, and applying this to the metallic foil used as a charge collector, making carry out solvent volatilization, and forming in a paint film object. The sintering method is the approach of making a pellet type carry out elevated-temperature sintering, and forming an electrode object ingredient in it after pressing, with electric conduction material etc., at a sintering object. There is also the approach of carrying out pressing of the paint film object formed by the paint film method, and making carry out elevated-temperature sintering and using as a sintering object in the sintering method. Generally, the sintering method can form a thin electrode about 20 to 40% to the same electric capacity as compared with a paint film method. Any of a paint film method and the sintering method may be used for formation of the negative-electrode object of this invention, and a positive-electrode object, and the combination of an approach of a different kind is sufficient.

[0017] When forming a negative-electrode object and a positive-electrode object by the sintering method, as for positive-electrode object thickness, it is preferably desirable to be referred to as 200-400 micrometers 40-1000 micrometers, and, as for negative-electrode object thickness, it is preferably desirable to be referred to as 50-150 micrometers 20-500 micrometers. The suitable value upper limit of electrode object thickness is based on the viewpoint which controls the rate of a volume ratio of the configuration member which a thickness suitable value minimum does not contribute to charge and discharge based on the viewpoint of full control of the capacity in high current density.

[0018] It is desirable to set positive-electrode object thickness to 40-300 micrometers, and to, set negative-electrode object thickness to 20-150 micrometers on the other hand, since it is the same as that of the sintering method when forming a negative-electrode object and a positive-electrode object by the paint film method.

[0019] In addition, the solid polymer electrolyte which made the nonaqueous electrolyte which dissolved the lithium compound in the organic solvent, or the organic solvent in which dissolution or a lithium compound was dissolved for the lithium compound hold can be used for the electrolyte used for the lithium secondary battery of this invention. Its all are usable if the above-mentioned organic solvent and a lithium compound are used for this kind of cell.

[0020]

[Example] Example 1 (production of positive-electrode object) lithium-carbonate powder and cobalt carbonate powder were mixed so that it might become a mole ratio 1:1, and temporary baking was carried out at 800 degrees C among the atmospheric-air ambient atmosphere for 1 hour. Subsequently, this was ground, pressing of the spherical polymethylmethacrylate particle of 5 micrometers of mean diameters was mixed and carried out, it calcinated at 800 degrees C among the atmospheric-air ambient atmosphere for 10 hours, and the positive-electrode object with a diameter [ of 19mm ] and a thickness of 0.5mm was acquired.

[0021] (Production of a negative-electrode object) after calcinating the crystalline substance silicon powder (product made from High grade Chemistry) 80 weight section with a% [ of purity ] of 99.9, and a mean particle diameter of 1 micrometer, and 1100 degrees C of graphite / pitch mixture (mixture [ of the graphite 90 weight section and the pitch 10 weight section ], trade name GURAFITON, and Osaka -- Formation -- make) 20 weight sections under nitrogen-gas-atmosphere mind for 3 hours, it ground and raw material powder was obtained. The raw material powder 90 weight section and the n-



methyl-2-pyrrolidone solution (14 % of the weight) 70 weight section of polyvinylidene fluoride were mixed, it considered as the shape of a paste, and the part was stuck by pressure and dried by the pressure of 100g/m<sup>2</sup> after applying to the sheet made from polyethylene terephthalate. This was started to the disk type with a diameter of 19mm, it calcinated at 800 degrees C under nitrogen-gas-atmosphere mind for 3 hours, and the negative-electrode object with a thickness of 0.2mm was acquired.

[0022] (Production of a coin mold cell) The laminating of the acquired positive-electrode object and the two negative polar bodies each was carried out so that it might become electric parallel connection with the aluminium foil which is a positive-electrode charge collector, the copper foil which is a negative-electrode charge collector, and a separator, and it contained with the sheathing can made from stainless steel, and the coin mold cell with a thickness of 1.8mm was produced. In addition, what carried out 1 mol/l dissolution of the 6 phosphorus-fluoride lithium was used for the mixed solvent (volume ratio 1:1) of ethylene carbonate and dimethyl carbonate at the electrolytic solution.

[0023] (Evaluation of a coin mold cell) Charge and discharge were repeatedly performed among 4.1V-2.5v, and the variation and discharge capacity of cell thickness accompanying charge and discharge were measured. The variation of cell thickness is a ratio to thickness at the time of discharge termination of the thickness variation at the time of charge and discharge, and it considered as the average of 10 cycle at first. The variation of cell thickness was about 5%, and the discharge capacity after 30 cycles was about 85% of first time discharge capacity.

[0024] If the thickness of an example 2 positive-electrode object and a negative-electrode object and laminating number of sheets were removed, the coin mold cell was produced by the same approach as an example 1. Thickness of 0.3mm and a negative-electrode object was set to 0.1mm for the thickness of a positive-electrode object, the laminating of a positive-electrode object and the four negative polar bodies each was carried out, and the coin mold cell with a thickness of 3mm was produced. The variation of cell thickness was about 7%, and the discharge capacity after 30 cycles was about 90% of first time discharge capacity.

[0025] If the thickness of the example positive-electrode object of a comparison and a negative-electrode object and laminating number of sheets were removed, the coin mold cell was produced by the same approach as an example 1. Thickness of 0.2mm and a negative-electrode object was set to 0.2mm for the thickness of a positive-electrode object, the laminating of a positive-electrode object and the four negative polar bodies each was carried out, and the coin mold cell with a thickness of 3mm was produced. The variation of cell thickness was about 14%, and the discharge capacity after 30 cycles was about 70% of first time discharge capacity.

[0026] Examples 1 and 2 produce a thin cell for the thickness of a negative-electrode object as below one half of the thickness of a positive-electrode object, and show the comparatively good cycle property. On the other hand, in the thickness of a negative-electrode object, the example of a comparison is producing the thin cell as a thickness EQC of a positive-electrode object, and the cycle property is inferior in it to examples 1 and 2. From the variation of cell thickness having been twice [ more than ] the examples 1 and 2, the example of a comparison is considered that the cycle property deteriorated for the increment in the contact resistance between the charge collector-electrode objects resulting from thickness change of the cell accompanying charge and discharge.

[0027]

[Effect of the Invention] Since this invention is constituted as explained above, it enables thin shape-ization of a lithium secondary battery, securing electric capacity.

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